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Imide/Arylene Ether Block Copolymers

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INTRODUCTION

As part of an effort to develop high performance structural resins with an attractive combination of properties, block copolymers containing an arylene ether and an imide segment were synthesized. Requirements for successful high performance composite matrix resins include stability in a hostile environment (aggressive solvents and high temperature), damage tolerance, good mechanical properties and low cost manufacturing.

Linear polyimides have excellent thermal stability, generally good environmental stability and high mechanical properties, but are often difficult to fabricate as structural adhesives or composite matrices. However, poly(arylene ethers) (PAE) have good thermal stability and mechanical properties and are easier to compression mold. The copolymers reported herein represent our initial work on imide/arylene ether copolymers which were synthesized in an attempt to take advantage of the attractive features of each system. A polymer previously reported¹ to have high toughness and low melt viscosity was selected as the arylene ether segment for use in this study. Two imide segments were studied, the first a well known amorphous polyimide with good physical and mechanical

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properties and the second, a semi-crystalline polyimide² with excellent properties that contains an arylene ether ketone segment similar in structure to that of the arylene ether block. Some preliminary information on these block copolymers has been reported^{3,4} previously.

Many copolymers containing an imide block and some other block have been reported. Most notable, the copolymers containing imide and siloxane blocks have received considerable attention.⁵⁻⁸ Other block copolyimides including poly(arylsulfone-imides),⁹ poly(imide-elastomers),¹⁰ poly(imide-urethanes),¹¹ poly(amide-imides),¹² poly(ester-imides),¹³ poly(imidine-imides)¹⁴ and copolymers of imide-aryl ether benzoxazoles^{15,16} have been reported.

EXPERIMENTAL

Monomers

2,2-Bis(4-hydroxyphenyl)propane (BPA) was obtained commercially and recrystallized from toluene to yield a white crystalline solid (mp 156-157°C). 1,3-Bis(4-fluorobenzoyl)-benzene (FFB) was synthesized as previously reported¹ and recrystallized from toluene to yield a white crystalline solid (mp 178-179°C). 4-Aminophenol was obtained commercially and vacuum sublimed to yield an off-white solid (mp 188-190°C). 4,4'-Oxydianiline (ODA) was obtained commercially and vacuum sublimed to yield an off-white solid (mp 190-192°C). Bis(4-aminophenoxy-4'-benzoyl)benzene (BABB) (mp 161.5-164°C) was obtained from Air Products and Chemicals, Inc. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained commercially and vacuum sublimed to yield a white crystalline solid (mp 224-226°C).

Oligomers

The amine-terminated poly(arylene ethers) (ATPAE) were synthesized as shown in Eq. 1, by aromatic nucleophilic substitution of FFB with BPA and 4-aminophenol in N,N-dimethylacetamide (DMAc) using potassium carbonate. The oligomers were prepared at two different calculated molecular weights (\bar{M}_n) by adjusting the monomer ratio (BPA/FFB) to 0.85 and 0.925 to provide \bar{M}_n s of 3110 and 6545 g/mole, respectively.

The following procedure is representative of ATPAE synthesis. FBB (22.562 g, 70.0 mmol), BPA (13.583 g, 59.5 mmol), 4-aminophenol (2.292 g, 21.0 mmol) and potassium carbonate (21.28 g, 154 mmol) in DMAc (115 ml) and toluene (40 ml) were stirred under a nitrogen atmosphere. The toluene/water azeotropic mixture was removed using a Dean-Stark trap as the reaction was heated to and held at 155°C for 16h. After filtering through sintered glass and neutralizing with acetic acid, the polymer was precipitated in water and subsequently washed with boiling water to provide ATPAE 3110 as an off-white solid in >95% yield.

The anhydride-terminated poly(amic acids) based on ODA and BTDA were prepared at two different \bar{M}_n s by adjusting the monomer ratio (ODA/BTDA) to 0.845 and 0.923 to provide \bar{M}_n of 3110 g/mole and 6545 g/mole, respectively as shown in Eq. 2. The synthesis for ODA/BTDA 3110 is given as an example. ODA (1.1844 g, 5.915 mmol) was dissolved in DMAc (17 ml) followed by addition of BTDA (2.2556 g, 7.0 mmol) with stirring for 3h at ambient temperature in a nitrogen atmosphere to form a clear yellow solution. The polyamic acid was then immediately polymerized with ATPAE. The anhydride-terminated poly(amic acids) based on BABB and BTDA were prepared at two different \bar{M}_n s in either DMAc or N-methyl-2-

pyrrolidinone (NMP) by adjusting the monomer ratio (BABB/BTDA) to 0.766 and 0.882 to provide \bar{M}_n of 3110 g/mole and 6545 g/mole, respectively as shown in Eq. 3.

Copolymers

The copolymers were prepared by adding a DMAc or NMP solution of ATPAE to the anhydride terminated poly(amic acid) reaction mixture. For example, to prepare ATPAE 3110//BABB/BTDA 3110, BTDA (1.1278 g, 3.5000 mmol) was added to a solution of BABB (1.3315 g, 2.6600 mmol) and DMAc (13.9 g) in nitrogen. The mixture was stirred 3h to form a clear solution. A solution of ATPAE 3110 (2.4593 g, 0.7908 mmol) in DMAc (13.9 g) was added to the poly(amic acid) solution to form a clear, viscous solution. Some reactions became very viscous and gelled within 15 min, but stirring overnight provided a clear viscous solution. These solutions were used to cast films which were thermally imidized. No gelation of the poly(amic acids) occurred using NMP or when the imide block was ODA/BTDA.

An alternate imidization procedure involved stirring the poly(amic acids) for 2h followed by the addition of toluene and heating to 155°C for 18h under a Dean-Stark trap. The yellow slurry was poured into water, the solid collected and subsequently washed in water. Drying in air at 100°C provided yellow powders that were used to prepare moldings.

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in $CHCl_3$ at 25°C for the ATPAE oligomers and poly(arylene ether) (FBB + BPA) and in DMAc or NMP at 25°C for the other polymers and copolymers. Differential

scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent T_g taken at the inflection point of the ΔT versus temperature curve. Torsional braid analysis (TBA) was performed at a heating rate of 3°C/min with the T_g taken at the peak of the damping curve. The number average molecular weight was determined for the amine-terminated poly(arylene ethers) (ATPAE) by amine group titration using a MCI Model GT-05 Autotitrator with 0.02 M HBr in glacial acetic acid as the titrant. The ATPAEs were dissolved in a 2:1 mixture of chlorobenzene and acetic acid.

Films

DMAc or NMP solutions (15% solids) of the polymers were centrifuged, the decantate doctored onto plate glass and dried at room temperature to a tack-free form in a dry air chamber. The films on glass were dried 1 h each at 100, 200 and 300°C. Mechanical tests were performed according to ASTM D882 on four specimens per test condition. Wide-angle X-ray scattering (WAXS) data was obtained on thin film specimens of the copolymers.

Moldings

The polymers were compression molded in a 1.25 in. square stainless steel mold using a hydraulic press equipped with electrically heated platens. Polymer filled molds were heated to 380°C, a pressure of 300 psi was applied and maintained for 0.5h, followed by cooling under pressure. Four compact tension specimens ~0.62 x 0.62 x 0.30 in. thick were machined from the 1.25 in. square molding and tested according to a known procedure.¹⁷

RESULTS AND DISCUSSION

ATPAEs with calculated \bar{M}_n s of 3110 and 6545 g/mole were prepared by offsetting monomer stoichiometry. These oligomers had η_{inh} of 0.16 and 0.29 dL/g and T_g of 133 and 146°C, respectively, as shown in Table I. When the oligomers were reacted with a stoichiometric amount of BTDA, the η_{inh} and the T_g increased as expected. The high η_{inh} obtained indicated that the calculated \bar{M}_n s were essentially correct. Subsequent end group analysis gave experimental \bar{M}_n s of 3600 g/mole and 7300 g/mole for the calculated \bar{M}_n s of 3110 g/mole and 6545 g/mole, respectively.

Table I also shows data for the homopolymers and 1:1 physical blends of the PAE with each polyimide prepared by mixing DMAc solutions of each. Both blend solutions phase-separated with the PAE migrating to the bottom phase and the poly(amic acid) migrating to the top phase. Small films cast from thoroughly mixed, cloudy solutions and cured to 300°C for 1h appeared to be completely phase separated. All polymers shown in the table are amorphous except the BABB/BTDA which has a T_m of 350°C.

Eight different block copolymers were prepared from reaction of the ATPAEs and the imide oligomers shown in Table II. The first four copolymers, that were prepared in DMAc only, contained imide blocks of ODA/BTDA while the last four contained BABB/BTDA imide blocks and were prepared in both DMAc and NMP. The ATPAE 6545//ODA/BTDA 6545 copolymer with $\eta_{inh} = 1.37$ dL/g was prepared using a stoichiometric ratio of oligomers. This polymer had a molecular weight too high to be easily compression molded (e. g. high melt viscosity), so the remaining copolymers utilizing the ODA/BTDA block were prepared at a 1.5% offset in stoichiometry favoring the ODA/BTDA oligomer. The resulting decrease in

molecular weight as evidenced by η_{inh} was larger than expected but tough, creasible films were formed. The ATPAE//BABB/BTDA copolymers shown in Table II were prepared using a stoichiometric ratio of oligomers to produce poly(amic acids) with η_{inh} s ranging from 0.63 to 0.89 dL/g in DMAc and from 0.90 to 1.73 dL/g in NMP.

The cured copolymers were characterized by DSC and these results are also shown in Table II. The ODA/BTDA containing copolymers with longer imide blocks show two T_g s, at temperatures slightly higher than the PAE and lower than the imide homopolymer T_g s. This indicates only a partial compatibility of the different blocks in the copolymer. The copolymers with the shorter ODA/BTDA block displayed only the lower T_g . The BABB/BTDA imide was chosen for further work because of its exceptional mechanical properties and since it contains an arylene ether ketone segment similar to the PAE, which was expected to improve the block compatibility of the copolymers. These copolymers had T_g s ranging from 165-175°C except for the ATPAE 6545//BABB/BTDA 6545 prepared in NMP which had T_g s at 164 and 220°C. The copolymers were semi-crystalline with T_m shown in parenthesis.

The last column in Table II shows transitions as measured by TBA, which measures a thermomechanical softening of the polymer compared to a purely thermal measurement of differential scanning calorimetry. In essentially every case this transition is different from the DSC T_g . For the first four copolymers which contain only amorphous blocks, the major TBA transitions appears either near the T_g of the major component (267°C when the major component is imide and 176°C when the major component is arylene ether) or as an average of the two homopolymer T_g s (216°C and

214°C) when each component is present in equal amounts. However, the TBA peaks were broader than for typical homopolymers and had a shoulder present near the T_g of the minor component. The last four copolymers in the table, which have a semi-crystalline imide block, display a wide range of TBA transitions (168 to 249°C). The ATPAE 3110//BABBB/BTDA 3110 gives one peak in the damping curve indicating a transition at 193°C which was approximately the average transition for the homopolymers. The ATPAE 3110//BABBB/BTDA 6545 displayed a transition at 249°C, higher than either homopolymer T_g . This transition must be influenced by the rigidity in the crystalline regions of the PI, since the imide segment is present in twice the amount as the PAE. The ATPAE 6545//BABBB/BTDA 3110 had a transition at 185°C, slightly higher than the calculated T_g from the rule of mixtures (177.4°C). The ATPAE 6545//BABBB/BTDA 6545 displayed two peaks in the damping curve at 168 and 205°C. These transitions are approximately 15°C above and below the T_g s of the PAE and PI, respectively indicating some incompatibility between the blocks at this molecular weight level.

The copolymers containing the BABBB/BTDA blocks displayed melting points in DSC so they were further analyzed by wide angle X-ray scattering. This data indicated that block copolymer films cured 1h at 300°C were semi-crystalline. Furthermore, copolymers with longer imide blocks or higher imide content had more intense and sharper peaks indicating more crystallinity than the others. Figure 1 shows the X-ray diffraction pattern for ATPAE 3110//BABBB/BTDA 3110 and is representative of the diffraction pattern for the other copolymers containing BABBB/BTDA. The peak positions are essentially identical to those of the BABBB/BTDA homopolymer with minor differences in sharpness and intensity.

Thin films of the homopolymers and copolymers were tested for mechanical properties and results are shown in Table III. Tensile strength, tensile modulus and film elongation were measured at room temperature (RT), 93°C and 177°C. In general, unoriented films of the imide homopolymers have high tensile strength and modulus and low elongation while the PAE has lower strength and modulus and very high elongation. Except for the films with the textured surface, presumably due to incompatibility of the blocks, the block copolymer films seem to follow a rule of mixtures weighted average for tensile strength and modulus when tested at RT and 93°C. That is, copolymers with longer imide blocks produced higher strength and modulus than those with longer arylene ether blocks. When testing at 177°C, the copolymers gave very poor properties due undoubtedly to the low T_g (~155°C) arylene ether block.

The block copolymers with imide blocks of BABB/BTDA were prepared as a fine, yellow powder by solution imidization, molded into compact tension specimen and tested for fracture toughness and energy. Data for these tests are shown in Table IV. Critical stress intensity factor (K_{Ic}) ranges from 3370 to 5070 psi • in^{1/2} while critical strain energy release rate (G_{Ic}) ranges from 22 to 67 in-lbs/in². The failed specimens exhibited a fracture surface that was highly crazed with evidence of pronounced polymer yielding. The FBB/BPA has the highest values. Since G_{Ic} equals K_{Ic} divided by the square of the film modulus, there is not a direct relation of K_{Ic} to G_{Ic} but the same general trend is present in both measurements. Results for each measurement fall below a rule of mixtures weighted average but the copolymers are still extremely tough materials, with the higher values corresponding to copolymers with higher molecular weight blocks.

Conclusions

Two series of block copolymers were prepared using an arylene ether block and either an amorphous or crystalline imide block. Copolymers with shorter blocks were more compatible than copolymers with longer blocks. Homopolymer blends were completely incompatible and phase separated upon mixing solutions and casting films. Copolymers containing a crystalline imide block were crystalline as-prepared but the crystallinity was unrecoverable by annealing after heating above the T_m . Film properties appear to follow a rule of mixtures weighted average while polymer toughness was below this average but still extremely high.

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TABLE I. CHARACTERIZATION OF OLIGOMERS AND POLYMERS

Oligomer or Polymer	η_{inh} , dL/g ^a	DSC T _g (T _m), °C ^b
ATPAE 3110	0.16 (CHCl ₃)	133
ATPAE 6545	0.29 (CHCl ₃)	146
ATPAE 3110/BTDA	0.79 (DMAC)	165
ATPAE 6545/BTDA	1.10 (DMAC)	162
ODA/BTDA	1.59 (DMAC)	278
BABB/BTDA	0.80 (DMAC)	222 (350)
FBB/BPA	0.70 (CHCl ₃)	155
ODA/BTDA + FBB/BPA (blend)	--	155, 222 (361)
BABB/BTDA + FBB/BPA (blend)	--	168, 265

^aMeasured at 25°C and 0.5% concentration^bMeasured at a heating rate of 20°C/min after curing 1 h at 300°C

TABLE II. CHARACTERIZATION OF BLOCK COPOLYMERS

Copolymer	Poly(amic acid) DMAc	η_{inh} , dL/g ^a NMP	DSC $T_g(T_m)$, °C ^b DMAc NMP	TBA Transition, °C ^c
ATPAE 3110//ODA/BTDA 3110	0.46	--	168	216
ATPAE 3110//ODA/BTDA 6545	0.50	--	167,265	267
ATPAE 6545//ODA/BTDA 3110	0.38	--	164	176
ATPAE 6545//ODA/BTDA 6545	0.37(1.37)	--	171,265	214
ATPAE 3110//BABB/BTDA 3110	0.63	0.90	175	193
			(354)	(338,352)
ATPAE 3110//BABB/BTDA 6545	0.87	1.73	170	249
			(354)	(358)
ATPAE 6545//BABB/BTDA 3110	0.81	1.00	168	185
			(353)	(335,352)
ATPAE 6545//BABB/BTDA 6545	0.89	1.03	165	168,205
			(335,350)	(343,355)

^aMeasured at 25°C and 0.5% concentration^bMeasured at a heating rate of 20°C/min after curing 1 h at 300°C^cMeasured at a heating rate of 3°C/min after curing 1 h at 300°C

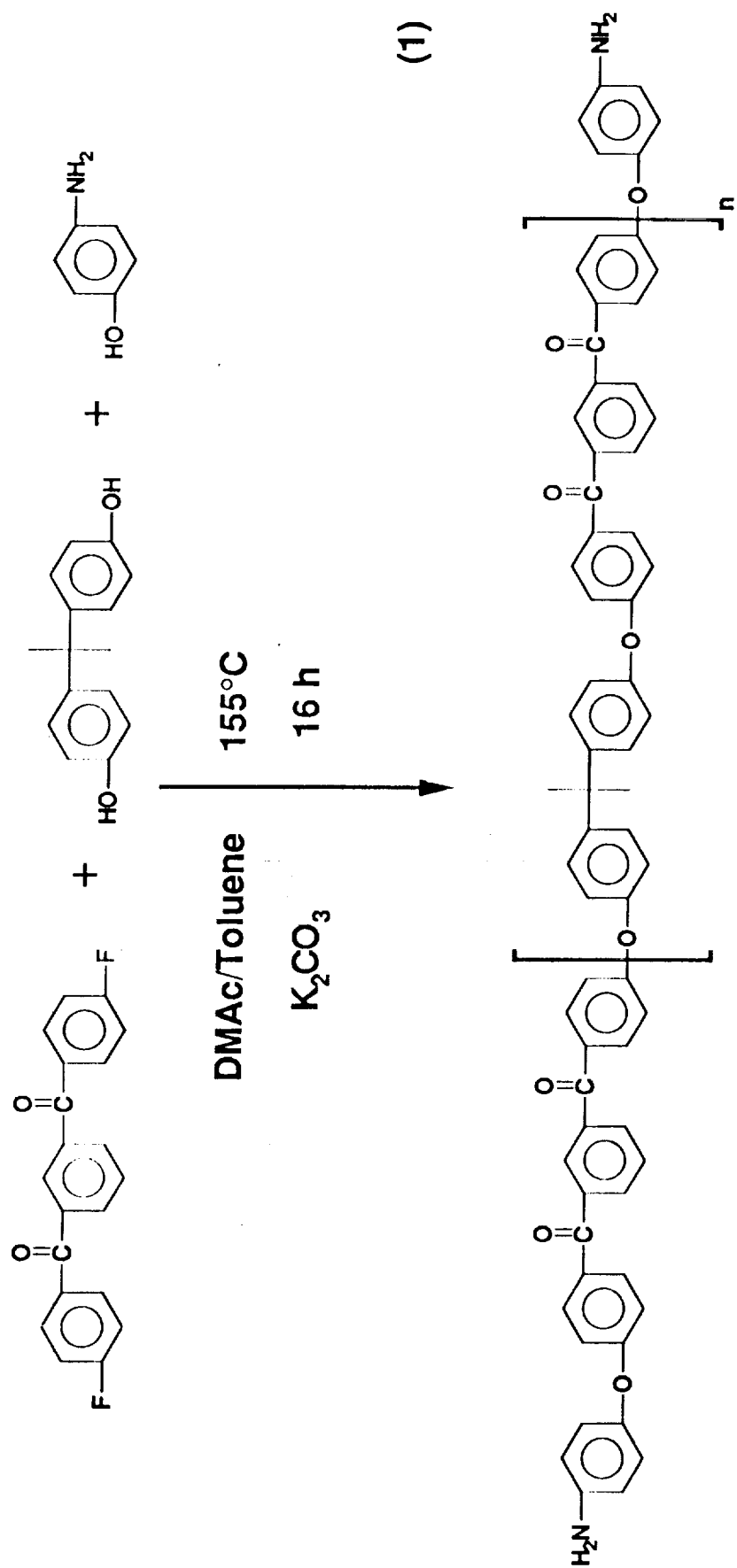
TABLE III. FILM PROPERTIES

Polymer	Tensile Strength, Ksi (Modulus, Ksi)[Elongation, %]		
	RT	93°C	177°C
ATPAE 3110/BTDA	10.9 (367) [4.0]	9.1 (333) [3.3]	1.2 (124) [80]
ATPAE 6545/BTDA	11.1 (367) [5.7]	8.5 (329) [5.2]	-- (--) [>100]
ATPAE 3110//ODA/BTDA 3110	14.1 (415) [4.9]	11.7 (400) [5.2]	3.8 (158) [10.3]
ATPAE 3110//ODA/BTDA 6545	16.2 (431) [5.7]	13.0 (389) [5.3]	6.2 (50) [19.1]
ATPAE 6545//ODA/BTDA 3110*	5.8 (321) [1.9]	4.2 (268) [1.9]	-- (--) [--]
ATPAE 6546//ODA/BTDA 6545*	11.2 (324) [4.6]	9.4 (299) [4.6]	3.9 (60) [17.7]
ATPAE 3110//BABBB/BTDA 3110	15.0 (514) [3.5]	12.7 (449) [3.2]	3.4 (135) [38]
ATPAE 3110//BABBB/BTDA 6545	16.2 (535) [3.8]	14.5 (516) [3.7]	5.9 (304) [30]
ATPAE 6545//BABBB/BTDA 3110	13.2 (435) [8.1]	10.5 (433) [16.1]	1.4 (36) [74]
ATPAE 6545//BABBB/BTDA 6545	14.2 (519) [4.3]	10.9 (437) [3.2]	2.7 (114) [49]
ODA/BTDA	19.5 (526) [14.6]	15.7 (393) [24.4]	9.6 (290) [18.2]
BABBB/BTDA	22.0 (630) [8.3]	-- (--) [--]	15.2 (540) [21]
FBB/BPA	12.7 (381) [136]	7.6 (340) [124]	-- (--) [--]

*Textured, orange peel surface

TABLE IV. FRACTURE TOUGHNESS AND ENERGY OF POLYMERS

Copolymer	Fracture Toughness (K_{Ic}), psi • in. ^{1/2}	Fracture Energy (G_{Ic}), in.-lbs/in. ²
ATPAE 3110//BABB/BTDA 3110	3370	22
ATPAE 3110//BABB/BTDA 6545	3900	28
ATPAE 6545//BABB/BTDA 3110	3930	36
ATPAE 6545//BABB/BTDA 6545	4760	44
BABB/BTDA	4890	38
FBB/BPA	5070	67



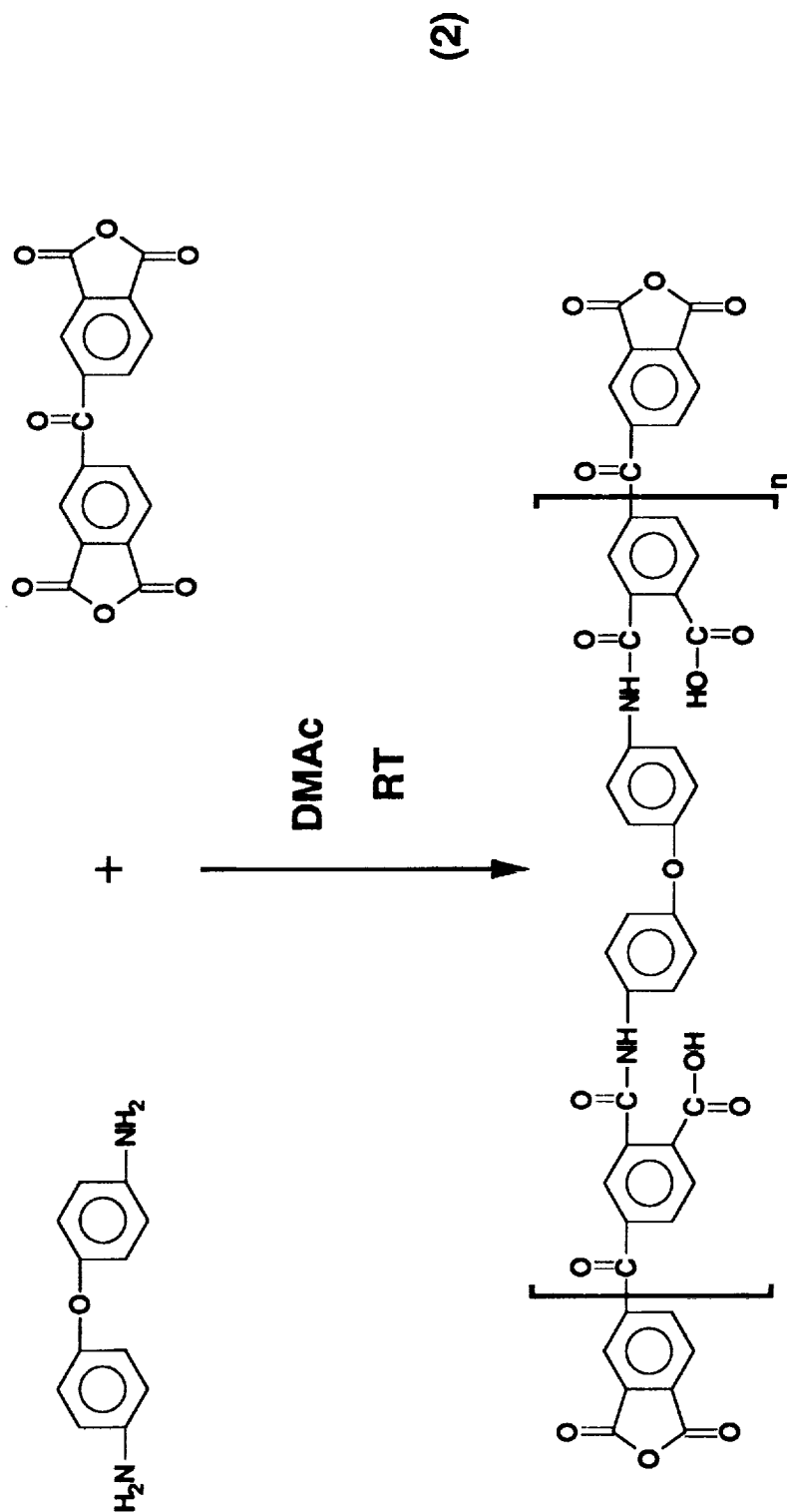
ATPAE

$\bar{M}_n = 3110 \text{ g/mole}$ and $\bar{M}_n = 6545 \text{ g/mole}$

$r = 0.850$

$r = 0.925$

$r = \text{ratio of BPA to FBB}$



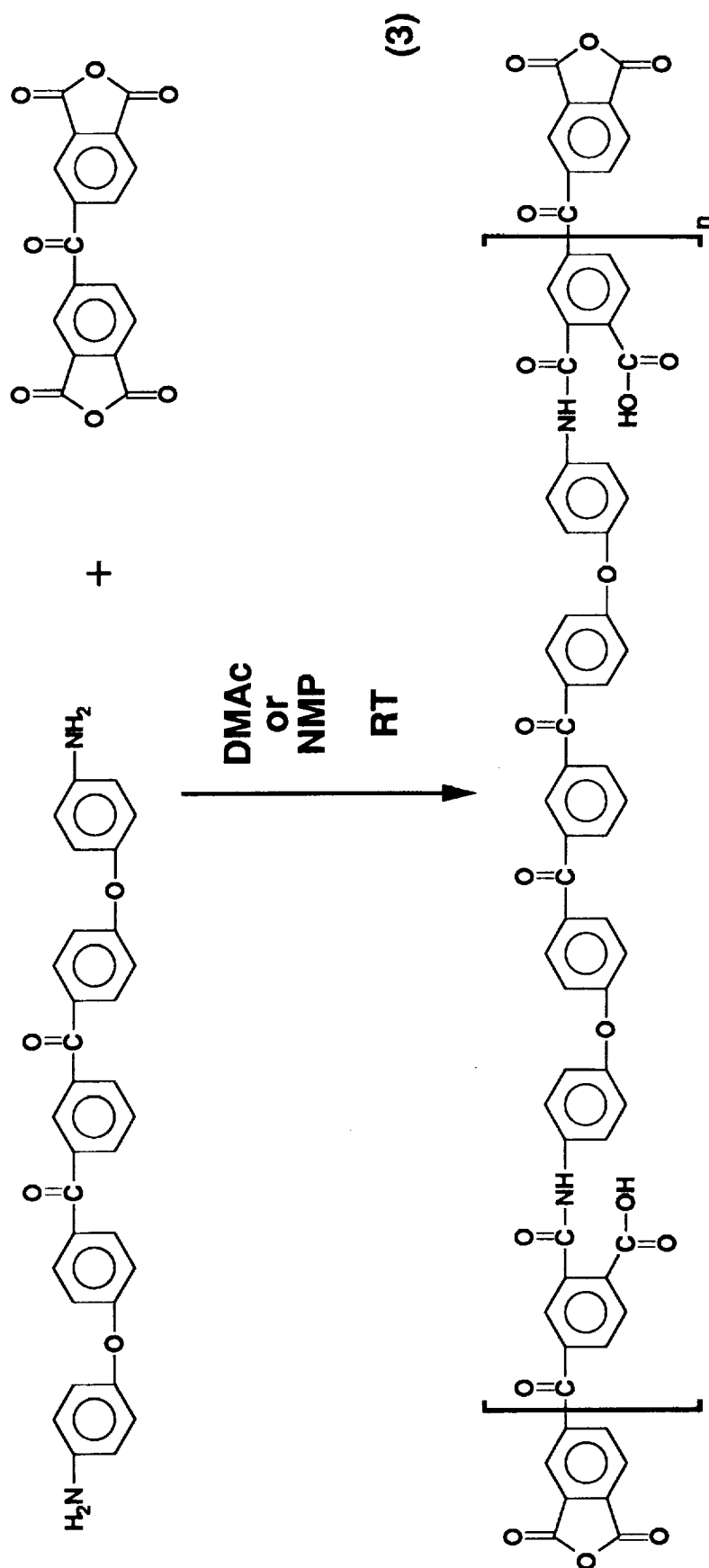
ODA/BTDA AA

$\overline{M}_n = 3110 \text{ g/mole}$ and $\overline{M}_n = 6545 \text{ g/mole}$

$r = 0.845$

$r = 0.923$

$r = \text{ratio of ODA to BTDA}$



BABB/BTDA AA

$\bar{M}_n = 3110$ g/mole and $\bar{M}_n = 6545$ g/mole

$r = 0.766$

$r = 0.882$

$r = \text{ratio of BABB to BTDA}$

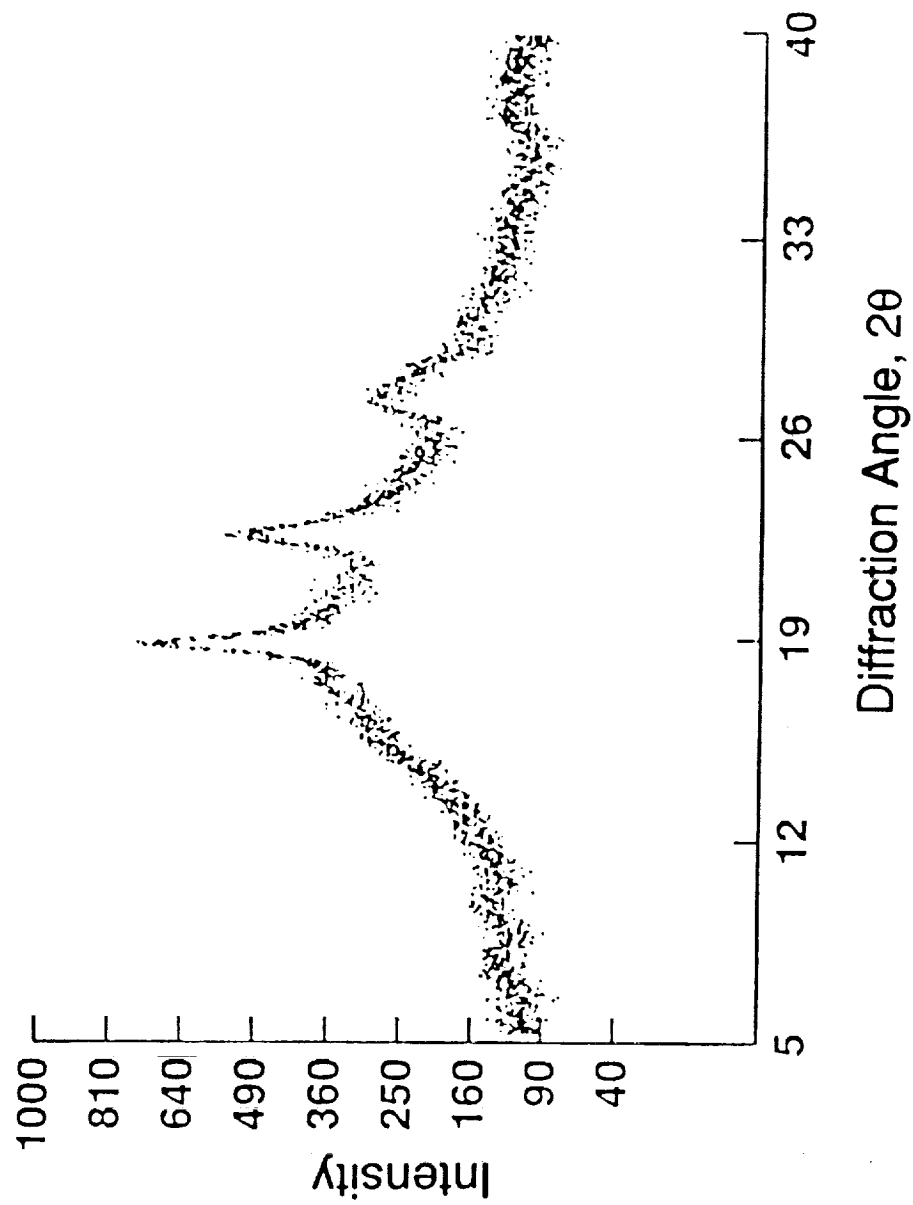


Figure 1. X-ray diffraction pattern for ATPAE 3110//BABBB/BTDA 3110 copolymer film.



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16. Abstract Two series of imide/arylene ether block copolymers were prepared using an arylene ether block and either an amorphous or semi-crystalline imide block. The resulting copolymers were characterized and selected physical and mechanical properties were determined. These results, as well as comparisons to the homopolymer properties, are discussed.		
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